PART ONE
CONTRIBUTION TO THE MULTIPLANAR ISOMERISM OF CYCLOHEXANES

PART TWO
RESTRICTED ROTATION IN NAPHTHYLAMINES

BY

ARNOLD HENRY ANDEREGG

B.A., University of Montana, 1940

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE COLLEGE OF THE
UNIVERSITY OF ILLINOIS, 1950

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ACKNOWLEDGMENT

The author desires to express his appreciation to Professor Roger Adams for his interest, advice and encouragement during the course of these studies. He also wishes to thank Dr. L. E. Miller and Dr. E. R. Alexander for their helpful suggestions.

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PART ONE

CONTRIBUTION TO THE MULTIPLANAR ISOMERISM OF CYCLOHEXANES

Introduction

Absolute chemical evidence of the existence of strainless isomeric forms of the cyclohexane ring has been the goal of numerous investigators. Isolation of two forms of 4-methylcyclohexane-1,1-dicarboxylic acid was reported by Desai (1) in 1942. It was the purpose of this present investigation to prepare the acids reported by Desai in order to investigate further their properties.

Discussion of Results

The compound, 4-methylcyclohexane-1-carboxy-1-acetic acid, was prepared by condensation of 4-methylcyclohexanone with ethyl cyanoacetate followed by hydrolysis of the hydrogen cyanide addition product. The resulting *cis-trans* isomers were separated by fractional precipitation from benzene. Bromination of the higher-melting, less-soluble form gave an impure sample of α-bromo-4-methylcyclohexane-1-carboxy-1-acetic acid and a pure sample of the anhydride of the α-bromo acid. Desai reported a pure α-bromo acid and the β-lactone of 4-methylcyclohexane-1-carboxy-1-acetic acid as products during the bromination. Alkaline hydrolysis of both the impure α-bromo acid and the pure α-bromo anhydride gave α-hydroxy-4-methylcyclohexane-1-carboxy-1-acetic acid. Numerous and varied unsuccessful attempts to oxidize the α-hydroxy acid to corresponding 4-methylcyclohexane-1,1-dicarboxylic acid were made. However, permanganate oxidation of the barium salt gave a very small amount of one of the acids reported by Desai.

The more-soluble, lower-melting isomer of 4-methylcyclohexane-1-carboxy-1-acetic acid was found extremely difficult

to obtain in a pure state. No reactions were attempted with this isomer.

The results of this investigation do not form a basis for either confirming or denying Desai's results.

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PART TWO

RESTRICTED ROTATION IN NAPHTHYLAMINES

Introduction

Comparison of the half-life periods of racemization of the optically active molecules, N-succinyl-1-methylamino-2-methylnaphthalene and N-succinyl-1-methylamino-2-methyl-4-chloronaphthalene, has shown the former to be more optically stable (1). In the present investigation an attempt has been made to prepare the 4-bromo and 4-nitro analogues in order to observe their effect on the optical stability of the molecule.

Discussion of Results

It was found in the previous work (1) that the half-life period of racemization of N-succinyl-1-methylamino-2-methylnaphthalene in boiling *n*-butanol was 5.7 hours as compared with 4.1 hours for the 4-chloro analogue. In this investigation the half-life period of the 4-chloro compound was found to be 3.35 hours in boiling *n*-butanol. The 4-bromo analogue was prepared from 1-amino-2-methylnaphthalene by acetylation, bromination, deacetylation, methylation and succinylation, followed by resoluton through fractional precipitation of the cinchonidine salt. Its half-life period of racemization was found to be 3.2 hours in boiling *n*-butanol.

The preparation of the 4-nitro analogue was unsuccessful. A compound which analyzed correctly for a dinitro- analogue was prepared by nitration of N-succinyl-1-methylamino-2-methylnaphthalene. This molecule was resolved and racemized. In boiling *n*-butanol it was totally racemized in twenty minutes.

A comparison of the respective rates of racemization of the compounds noted above would indicate that the more electronegative substituents cause greater optical instability.

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VITA

The author was born in Helena, Montana, on May 9, 1916. All his elementary schooling was received in the Helena schools. In September, 1936, he entered the State University of Montana from which he was awarded the degree of Bachelor of Arts in Mathematics in 1940. While attending Graduate College at the same school, he was called to duty with the United States Army in January, 1941. He served as an Infantry officer both in the United States and in the Asiatic-Pacific combat area until June, 1946, when he entered the Graduate College of the University of Illinois. He held an appointment as Assistant in Chemistry from September, 1946, to August, 1948, and a University of Illinois Fellowship from September, 1948, to June, 1949.

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